

Studies on Electrochromism of Chemically Deposited Nickel Oxide Thin Films

Julijana Velevska,^{1*} Margareta Pecovska-Gjorgjevich,¹
Metodija Najdoski² and Nace Stojanov¹

¹*Institute of Physics, ²Institute of Chemistry, Faculty of Natural Sciences and Mathematics,
St. Cyril and Methodius University, P.O. Box 162, Skopje 1001, Macedonia*

**Corresponding author. E-mail address: julev@pmf.ukim.mk*

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Abstract

In this work, nickel oxide (NiO_x) thin films were prepared from aqueous solution of nickel nitrate and carbamide. Those films were deposited onto fluorine doped tin oxide (FTO) coated glass substrates. An electrochromic test device (ECTD) was constructed by using these films as working electrodes, and FTO coated glass as an opposite electrode in alkaline medium of 0.1 M NaOH aqueous solution. The obtained nickel oxide films exhibited anodic electrochromism, changing color from transparent to dark brown. Various techniques were used for characterization of the films as x-ray diffraction (XRD), visible spectroscopy and electrochemical methods. The dependence of the optical density on the charge density was examined and the coloration efficiency was calculated from the optical density change. The time response was also determined.

Key Words: Chemical bath deposition; Electrochromism; Nickel oxide

Introduction

Optically active thin films coatings can alter their optical properties as a function of changes in external conditions. The changeable optical characteristics can be obtained by different physical and chemical processes in a large number of materials. These substances named chromogenics, embrace both inorganic and organic materials. The mechanism responsible for the reversible variation of the optical properties of films may basically be divided in three different types: thermochromism, photochromism and electrochromism.

Electrochromism is the unique property of a material to change color reversibly, when a voltage is applied across it. Actually, this is potentially the most commercially useful form of chromism. An electrochromic process is complicated, and the electrochromism of the different materials is strongly related to the method of preparation, i.e. it is affected by structure, stoichiometry, binding conditions and water content in the films.

The various types of electrochromic substances can be divided into two classes: inorganic oxides and organic materials. Another classification

is related to the potential where coloration process occurs. Cathodically coloring materials possess a reduced colored state, i.e. they color at a negative potential, while anodically coloring materials are those with oxidized color state, i.e. they color when a positive potential is applied (Cerc Korosec and Bukovec, 2006).

Currently, the electrochromic properties of nickel oxide films are of great interest for applications as anodic material in electrochromic devices due to its high efficiency, low cost, and good stability. There are varieties of techniques for preparation of nickel oxide films. Usually they are prepared by cathode electrodeposition (Ragan et al., 1998), sputtering (Kitao et al., 1995), spray pyrolysis (Arakaki et al., 1995), evaporation (Nagai, 1993], chemical vapour deposition (Maruyama and Arai, 1993), sol – gel technique (Surca et al., 1996) etc.

Recently, soft solution processing (SSP) has raised considerable attention, as it is one – step, environment friendly, and low – energy consumption process among existing techniques of preparing thin films (Yoshimura, 1998). As a branch of SSP, chemical bath deposition (CBD) has been well developed to fabricate the large – area semiconductor thin films in view of many advantages: it does not require sophisticated equipment like vacuum system and other expensive instruments; the starting chemicals are commonly available and cheap; various substrates including insulators, semiconductors or metals can be used; the preparation parameters are easily controlled, (Mane and Lokhnade, 2000), (Cheng et al., 2003), (Todorovski et al., 2006), (Ristova et al., 2002), (Igwe et al., 2009). As in any chemical method, composition of solution and thermal conditions has a strong effect on film properties. This paper presents investigations of electrochromic properties of thin

nickel oxide films prepared by CBD technique from aqueous solution of nickel nitrate and carbamide.

Materials and methods

Nickel oxide films investigated in this work were prepared by CBD method onto fluorine doped tin oxide (FTO) coated glass substrates. The CBD technique is very simple and does not require special set – up. A 100 ml – laboratory beaker was used for deposition on four substrates. An aqueous solution containing 1 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3 g carbamide in 80 ml deionized water was placed in the beaker. Then the substrates were vertically introduced into the solution. The temperature was adjusted and kept at 95 °C. After 30 min, the substrates with deposited films were taken out, washed under strong flash water, rinsed with deionized water and dried in air. The thickness of the obtained films, measured with Dectak Stylus Profilometer, was 200 nm.

The composition and crystal structure of the films were studied by x-ray diffraction (XRD) by Cu K_α radiation at wavelength $\lambda = 1.54 \cdot 10^{-10}$ m, with a Siemens D – 500 diffractometer.

In order to examine the electrochromic behavior of the obtained films, an electrochromic test device (ECTD) was designed. It consisted of a transparent cuvette with a 0.1 M NaOH aqueous solution electrolyte in which two electrodes were immersed. The working electrode represented the nickel oxide thin film onto FTO coated glass, whereas counter electrode was FTO coated glass. Figure 1 depicts the cross section of the so – designed ECTD.

The optical properties of the nickel oxide films were studied using Varian CARY 50 Scan UV – Visible spectrophotometer, in the wavelength range from 320 to 820 nm. The visible transmission spectra were taken in-situ (the NiO_x film incorporated as a working electrode into the ECTD) in both, the

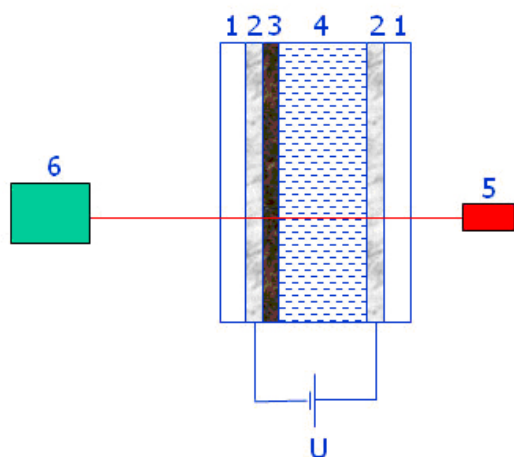


Figure 1 Cross-section of the ECTD: 1 – glass, 2 – FTO, 3 – NiO_x film, 4 – electrolyte, 5 – light source, 6 – light detector.

completely bleached and colored states of the film. The blank probe data were taken as the working electrode from the ECTD was replaced with FTO/glass electrode, so that the transmission spectrum could be normalized to 100%. The coloration and the bleaching of the nickel oxide thin films were performed by application of a voltage +1 V and –1 V respectively.

From the transmittance data and the film thickness ($d = 200$ nm) we determined the absorption coefficient from:

$$\alpha = \frac{1}{d} \ln \frac{1}{T}$$

The optical gap E_g of the film in the bleached and colored states was evaluated from the standard expression (Liu et al., 2005):

$$\alpha \cdot h \cdot \nu \propto (h \cdot \nu - E_g)^m$$

where $h\nu$ is the energy of the incident photon, E_g is the optical energy gap and m is the number which characterizes the optical processes.

The value of m is 1/2 for the direct allowed transition, 3/2 for forbidden direct allowed transition and 2 for indirect allowed transition. When the straight portion of the graph of $(\alpha h\nu)^m$ against $h\nu$ is extrapolated to $\alpha = 0$ the intercept gives the transition band gaps.

The cyclic voltammetry measurements were carried out using computer linked three-electrode arrangement with platinum (Pt) as counter electrode and silver-silver chloride (Ag/AgCl) as a reference electrode in a potential range from –1 V to +1 V and back to –1 V versus the counter electrode. The voltage scan rate was 10 mV/s, and the film working area was 1 cm².

The dependence of the transmittance at 670 nm laser light versus the applied cyclic voltage from –1 V to +1 V and back to –1 V was studied with the following setup: light beam was directed to pass normally through the ECTD whereas a pin photodiode was mounted on the opposite side of the ECTD in order to receive the transmitted light signal through ECTD. The transmittance was determined by equation $T = I/I_0$, where I and I_0 are the photodiode current for a given voltage and the photodiode current from the fully bleached film, respectively. The transmittance of the film's fully bleached state was fixed to 100%. The film working area was 2.5 cm².

The most important parameter for the characterization of the electrochromic film is the coloration efficiency $CE(\lambda)$ of a unit area at a given wavelength. The coloration efficiency of the NiO_x was calculated from the optical density change $\Delta OD = \log T_b/T_c$ at wavelength 670 nm, and the charge density $\Delta Q/S$ during coloration after films were fully bleached:

$$CE(\lambda) = \frac{S \log(T_b/T_c)}{\Delta Q} \quad (1)$$

Where T_b and T_c are the transmittance (at wavelength 670 nm) of the fully bleached and colored states respectively, ΔQ is the ejected charge, determined by the applied current through the test device and the time of its application, and S is the active area of the electrochromic device.

Finally, the responsiveness of the films was examined in situ at wavelength 550 nm (white light), as a transmittance change due to abrupt voltage change between -2 V and $+2$ V. The transmission at 550 nm white light through the ECTD was registered with a pin photodiode, which served as a transmitted light-measuring unit.

Results and discussion

The prepared nickel oxide films by CBD

technique revealed anodic electrochromic behavior changing color from transparent to dark brown (Cerc Korosec and Bukovec, 2006). They could be repeatedly colored and bleached with alternative application of a positive and negative voltage respectively, versus a counter electrode.

The XRD pattern of the as deposited film onto FTO coated glass substrate is presented in Figure 2. The seven most distinct detected peaks were found to originate from the FTO substrate. The other three detectible peaks at: $2.31 \cdot 10^{-10}$ m, $2.096 \cdot 10^{-10}$ m, and $1.474 \cdot 10^{-10}$ m, were found to correspond to the nickel oxide. The conversion from D values to 2θ for these three peaks is given in Table 1. Diffraction peak at about $2\theta = 38.94^\circ$ is value reported for β - phase $\text{Ni}(\text{OH})_2$ [Ezema et

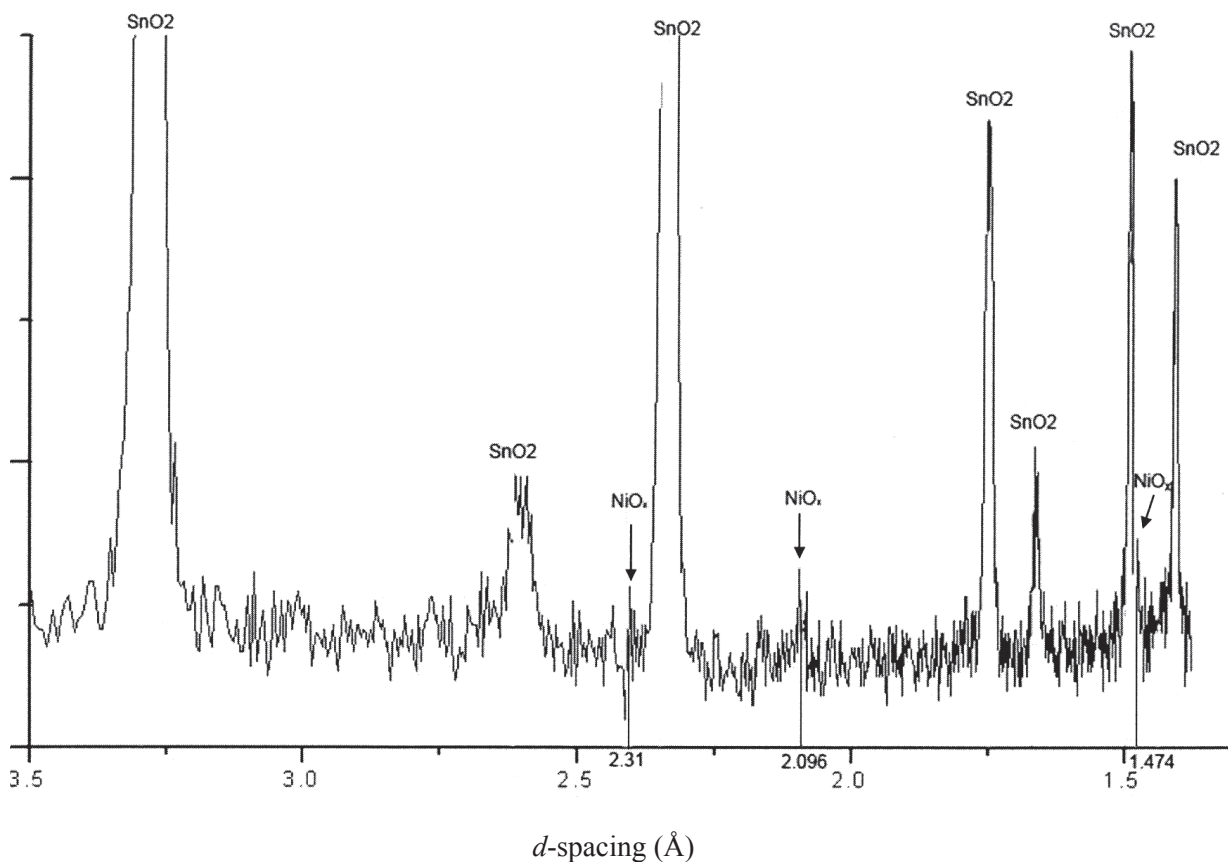


Figure 2 XRD pattern of a nickel oxide film onto FTO coated glass substrate.

Table 1 NiO peak identification and d spacing to 2θ conversio

Peaks	$d \cdot 10^{10}$ (m)	$2q$ (degrees)
1	2.31	38.94
2	2.096	43.11
3	1.474	62.98

al., 2008]. The diffraction peaks arising from NiO appear at about $2\theta = 43.11^\circ$ and 62.98° are values reported for cubic NiO [Jiao et al., 2003]. These indicate coexistence of β -Ni(OH)₂ and NiO phases.

Figure 3 presents photographs of NiO_x films in a) bleached and b) colored states, which were made ex situ. The films were first removed from the ECTD after bleaching (coloring), rinsed in distilled water, dried, and then photographed with a digital camera. One could notice significant difference between the colors of the films in both states.

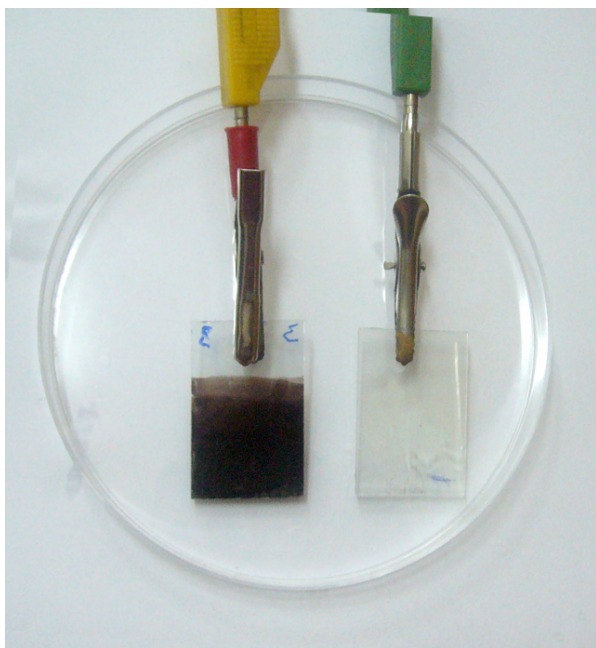
**Figure 3** Photographs of a NiO_x films in colored and bleached states.

Figure 4 shows the in situ optical spectra of the bleached and colored states of NiO_x films in the wavelength range from 320 to 820 nm. These data were taken relative to the FTO coated glass substrate. As can be seen in this figure, there is a significant difference in the transmittance between the colored and bleached states of the films.

Figure 5 shows the plot of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for both, bleached and colored states. A band gap is obtained from the intersection of the fitted straight line and the abscissa. The similar energy value of 3.26 eV and 3.21 eV for bleached and colored states of the films respectively was extracted. Comparing the results to the literature data (3.2 - 3.6 eV), (Wang et al., 2005; Subramanian et al., 2008; Sonavane et al., 2010), we find similar values with the same type of transition.

The current change in Figure 6 and the transmittance change at $\lambda = 670$ nm in Figure 7 are presented as a function of the voltage applied across the full device (Rubin et al., 1998). The ECTD was cycled over range ± 1 V. The voltage sweep rate of cycling was 10 mV/s. The transmittance at $\lambda = 670$ nm of the ECTD in a fully bleached state was taken to be 100%. The graph presents the histogram of $I-V$, which is due to the electrochromic behavior, whereas the transmittance (at $\lambda = 670$ nm) changed from 100% (normalized transmittance for the bleached state) to 40% corresponding to the colored state.

Figure 8 shows the graphical presentation of the optical density change (ΔOD) as a function of the charge density Q/S . Since ΔOD changes linearly with Q/S , the coloration efficiency (CE) can be determined from the slope of the straight line in Fig. 8. The coloration efficiency calculated from Equation 1 was found to be 40.6 cm²/C, which is good value compared with those obtained for the NiO_x films deposited by other techniques (Ferreira

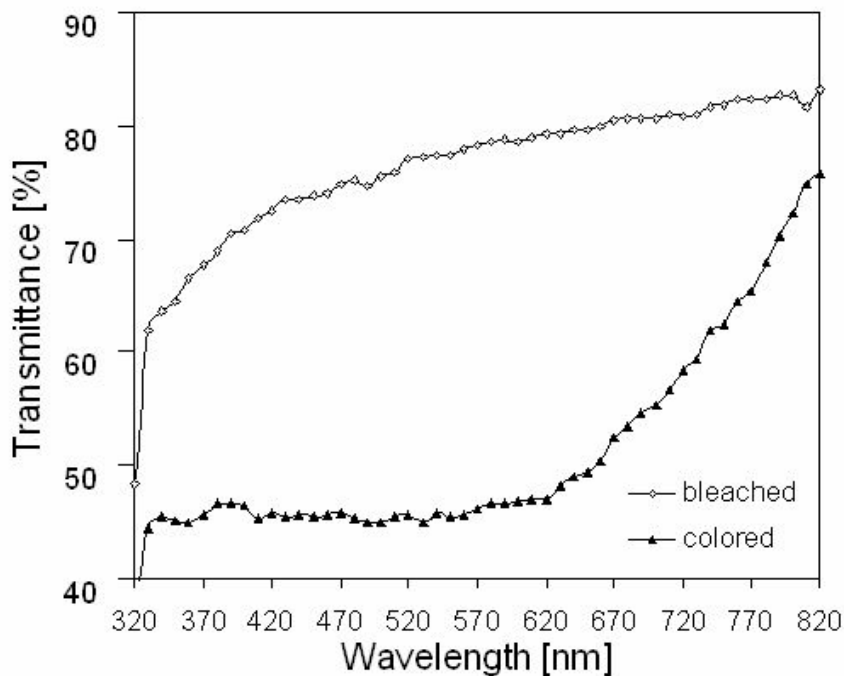


Figure 4 Optical transmission of the NiO_x films in the bleached and colored states in the visible part of the spectrum. The data were taken relative to the FTO coated glass substrate.

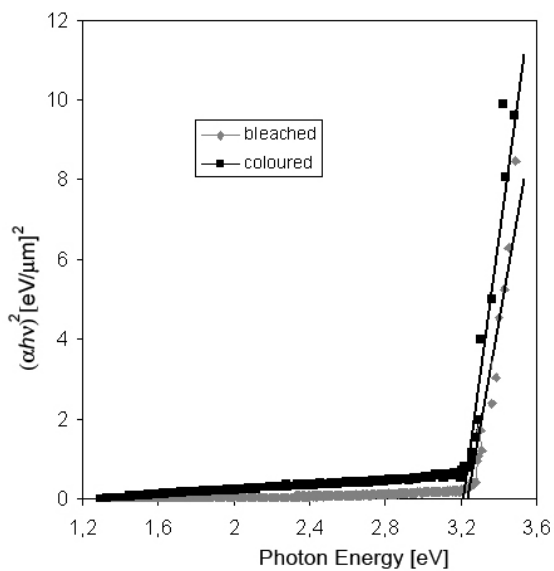


Figure 5 Plots of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for NiO_x films in bleached and colored states.

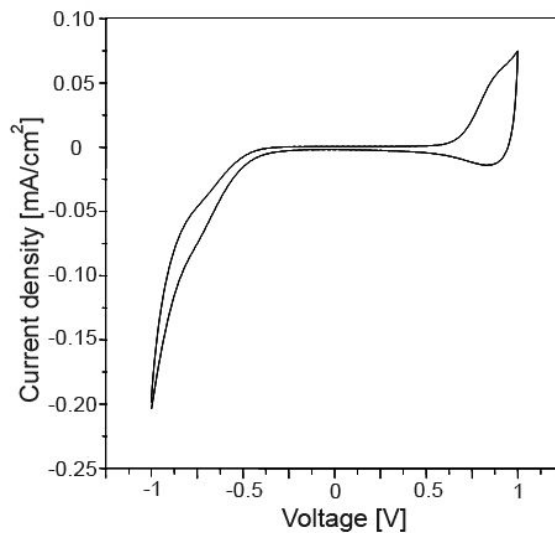


Figure 6 A cycling voltammogram of the NiO_x films recorded from -1 V to +1 V and back to -1V in a three-electrode arrangement with Pt as counter electrode and an Ag/AgCl as a reference electrode in a 0.1 M NaOH aqueous solution.

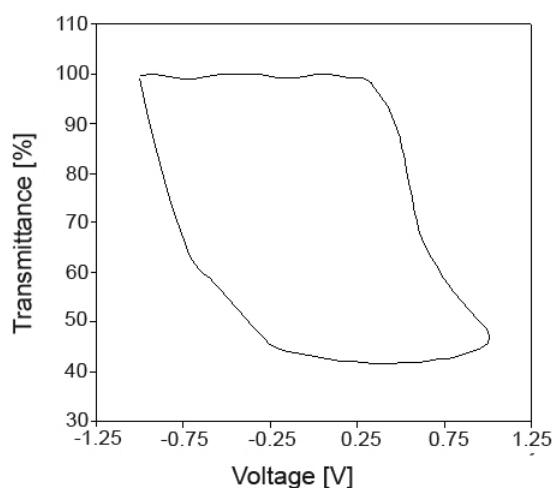


Figure 7 Presentation of the transmittance change at 670 nm of the NiO_x films recorded from -1 V to $+1$ V and back to -1 V against FTO electrode.

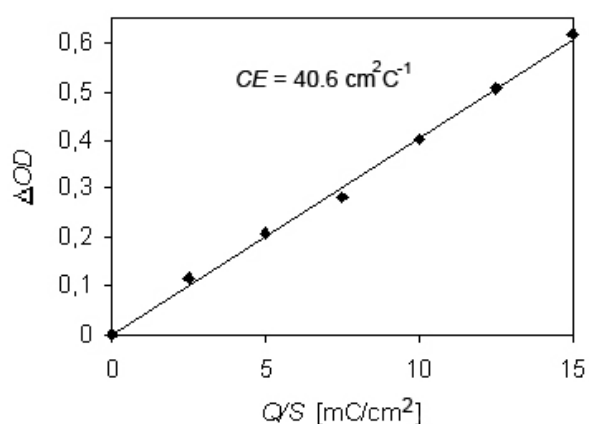


Figure 8 The dependence of the optical density on charge density.

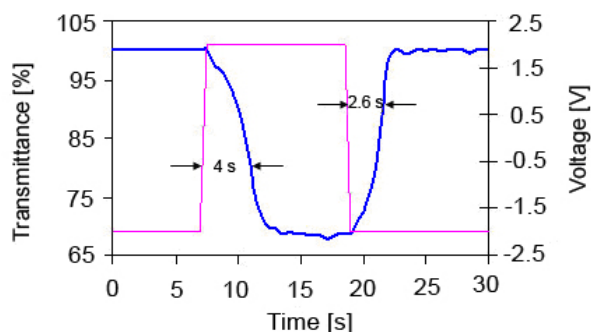


Figure 9 The time response of the transmittance recorded at 550 nm. The applied potential is switched between -2 V and $+2$ V.

et al., 1996; Lechner and Thomas, 1998; Kadam and Patil, 2001; Ristova et al., 2002; Velevska and Ristova, 2002; Park et al., 2004).

In order to examine the time response (coloration and bleaching times), the transmittance for white light ($\lambda = 550$ nm) was measured in situ through the ECTD (Figure 9). The applied potential was switched between -2 V and $+2$ V. The transmittance of the ECTD at 550 nm in fully bleached state was normalized to 100%. The coloration and bleaching times, defined as the time to reach 2/3 of the final change in the transmittance (Cinnsealach et al., 1998), were found to be about 4 and 2.6 s, respectively. It means that NiO_x films prepared by CBD technique can reach their bleached state more rapidly than colored state. It could be explained with the lower conductivity of $\text{Ni}(\text{OH})_2$ (bleached state) than that of the NiOOH (colored state) (Ahn et al., 2002).

Conclusions

Nickel oxide thin films were deposited onto FTO coated glass substrates from aqueous solution of nickel nitrate and carbamide using CBD technique. The technique is simple, economic, and offers a possibility for large area depositions. The obtained films exhibited electrochromic behavior: they were colored at a positive potential, changing color from transparent to dark brown. The optical and the electrochromic properties of this material are convenient for visible light intensity modulation applications. Variations in the transmittance for 670 nm laser light due to the charge insertion/extraction of about 60% were achieved. Obtained nickel oxide films show fast response time (about 4 s for coloring and 2.6 s for bleaching). Finally, the coloration efficiency (at 670 nm) was found to be $40.6 \text{ m}^2/\text{C}$, which is good value compared with those obtained for the NiO_x films deposited by other techniques.

References

- Ahn, K.S., Nah Y. C., and Sung, Y. E. (2002) Thickness-dependent microstructural and electrochromic properties of sputter-deposited Ni oxide films. *Journal of Vacuum Science and Technology A* 20 (4): 1468-1474.
- Arakaki, J., Reyes, R., Horn M., and Estrada, W. (1995) Electrochromism in NiO_x and WO_x obtained by spray pyrolysis. *Solar Energy Materials and Solar Cells* 37: 33-41.
- Cerc Korosec, R. and Bukovec, P. (2006) Sol-Gel Prepared NiO thin films for electrochromic applications. *Acta Chimica Slovenica* 53: 136-147.
- Cheng, J., Fan, D. B., Wang, H., Liu, B. W., Zhang, Y. C. and Yan, H. (2003) Chemical bath deposition of crystalline ZnS thin films. *Semiconductor Science and Technology* 18: 676.
- Cinnsealach, R., Boschloo, G., Nagaraja, S., and Fitzmaurice, D. (1998) Electrochromic windows based on viologen - modified nanostructured TiO₂ films. *Solar Energy Materials and Solar Cells* 55: 215-223.
- Ezema, F. I., Ekwealor, A. B. C. and Osuji, R. U. (2008) Optical properties of chemical bath deposited nickel oxide (NiO_x) thin films. *Superficies Vacio* 21 (1): 6-10.
- Ferreira, F. F., Tabackniks, M. H., Fantini, M. C. A, Faria, I. C. and Gorenstein, A. (1996) Electrochromic nickel oxide thin films deposited under different sputtering conditions. *Solid State Ionics* 86-88: 971.
- Igwe, H. U., Ekpe, O. E, Ugwu, E. I. (2009) Effects of Thermal annealing on the optical properties of nickel oxide thin films prepared by chemical bath deposition technique. *Pacific Journal of Science and Technology* 10(2): 806-810
- Jiao, Z., Wu, M., Qin, Z., and Xu, H. (2003) The electrochromic characteristics of sol-gel-prepared NiO thin film. *Nanotechnology* 14: 458-461.
- Kadam, L. D. and Patil, P. S. (2001) Studies on electrochromic properties of nickel oxide thin films prepared by spray pyrolysis technique. *Solar Energy Materials and Solar Cells* 69: 361-369.
- Kitao, M., Izawa, K., and Yamada, S. (1995) Electrochromic properties of nickel oxide films prepared by introduction of hydrogen into sputtering atmosphere. *Solar Energy Materials and Solar Cells* 39: 115-122.
- Lechner, R. and Thomas, L. K. (1998) All solid state electrochromic devices on glass and polymeric foils. *Solar Energy Materials and Solar Cells* 54: 139-146.
- Liu, X., Qiu, G., Wang, Z., and Li, X. (2005) Rationally synthetic strategy: from nickel hydroxide nanosheets to nickel oxide nanorolls. *Nanotechnology* 16: 1400-1405.
- Mane, R. S. and Lokhande, C. D. (2000) Chemical deposition method for metal chalcogenide thin films. *Materials Chemistry and Physics*. 65: 1-31.
- Maruyama, T. and Arai, S. (1993) The electrochromic properties of nickel oxide thin films prepared by chemical vapor deposition. *Solar Energy Materials and Solar Cells* 30: 257-262.
- Nagai, J. (1993) Characterization of evaporated nickel oxide and its application to electrochromic glazing. *Solar Energy Materials and Solar Cells* 31: 291-299.
- Park, J. Y., Akn, K. S., Nah, Y. C., Shim, H. S., and Sung, Y. E. (2004) Electrochemical and electrochromic properties of Ni-oxide thin films prepared by a sol-gel method. *Journal of Sol-Gel Science and Technology* 31:

- 323-328.
- Ragan, D. D., Svedlindh, P., and Granqvist, C.G. (1998) Electrochromic Ni oxide films studied by magnetic measurements. *Solar Energy Materials and Solar Cells* 54: 247-254.
- Ristova, M., Velevska, J., and Ristov, M. (2002) Chemical bath deposition and electrochromic properties of NiO_x films. *Solar Energy Materials and Solar Cells* 71: 219-230.
- Rubin, M., Wen, S. J., Richardson, T., Kerr, J., Von Rottkay, K., and Slock, J. (1998) Electrochromic lithium nickel oxide by pulsed laser deposition and sputtering. *Solar Energy Materials and Solar Cells* 54: 59-66.
- Sonavane, A. C., Inamdar, A. I., Shinde, P. S., Deshmukh, H. P., Patil, R. S., and Patil, P. S. (2010) Efficient electrochromic nickel oxide thin films by electrodeposition. *Journal of Alloys and Compounds* 489(2): 667-673
- Subramanian, B., Mohamed Ibrahim, M., Senthilkumar, V., Murali, K. R., Vidhya, V. S., Sanjeeviraja, C. and Jayachandran M. (2008) Optoelectronic and electrochemical properties of nickel oxide (NiO) films deposited by DC reactive magnetron sputtering. *Physica B: Condensed Matter* 403 (21-22): 4104-4110
- Surca, A., Orel, B., Pihlar, B., and Bukovec, P. (1996) Optical, spectroelectrochemical and structural properties of sol-gel derived Ni-oxide electrochromic film. *Journal of Electroanalytical Chemistry* 408: 83-100.
- Todorovski, T., Najdoski, M., and Velevska, J. (2006) Chemical deposition of molybdenum oxide thin films from dimethyl sulfate bath. *International Journal of Pure and Applied Chemistry* 1(4): 549-552.
- Velevska, J. and Ristova, M. (2002) Electrochromic properties of NiO_x prepared by low vacuum evaporation. *Solar Energy Materials and Solar Cells* 73: 131-139.
- Wang, X., Song, J., Gao, L., Jin, J., Zheng, H., and Zhang, Z. (2005). Optical and electrochemical properties of nanosized NiO via thermal decomposition of nickel oxalate nanofibres. *Nanotechnology* 16: 37-39.
- Yoshimura, M. (1998) Importance of soft processing for advanced inorganic materials. *Journal of Materials Research* 13: 796-802.